MICROSTRUCTURAL AND COMPOSITIONAL ASPECTS OWING TO Mg AND B ADDITIVES IN SPRAY DEPOSITED SnO_2 THIN FILMS FOR ENHANCED LPG AND METHANE SENSING

Due to rapid industrialization accompanied by globalization, developing countries like India are now facing grave environmental crisis. The increasing environmental pollutants, effluents, toxic and inflammable gases, automobile exhaust etc are posing great threats to the healthy and sustained existence of flora and fauna all over the world. Air pollution is one of the most crucial current environmental problems, especially in urban areas. Hence the development of low cost gas sensors is of utmost interest among the researchers. Highly inflammable LPG being in common domestic usage and methane being a green house gas, their monitoring is of utmost importance and the development of durable, low cost sensors would make them reach common man.

The term thin film metal oxide gas sensor usually refers to metallic oxides formed on substrates like ceramic, glass, silicate or wafer. To these sensors, the gas simply gets adsorbed onto the material surface, changing the resistance which is highly dependent on the surface stoichiometry and additives. In the absence of gas the occurred sensing mode gets reversed and no permanent modification is demonstrated by the material. Hence properly manufactured solid-state sensors offer prolonged existence over repeated usage. Another feature of solid state sensor is that, the operating temperature of such a sensing material can be suitably changed in order to make them sensitive to different gases with the same device. In general, although the performance of solid state sensors is appreciated, there are many problems associated with the development of a acceptable stable material for attaining good sensitivity with precise selectivity. Recently, the emphasis is being given to the progress in the nano-scale area to exploit the unique properties due to the advantages of increased surface-to-volume ratio. Additionally, the sensor characteristics are found to be dependent on the material, microstructure and additives. This is one of the reasons why different materials and film preparation routes are exploited for the sensing of different gases. Although the oxides themselves are active for gas detection, they are rarely used in isolation due to the fact that their gas sensing characteristics can be greatly enhanced by doping.

The main objective of the work is to develop low cost reducing gas sensors with good sensitivity with selectivity. In the present investigation, transparent and conducting polycrystalline tin oxide thin films are deposited on glass substrate by inexpensive spray pyrolysis method and analysed for their LPG and methane gas detection capability. The effect of doping the material with low concentrations of magnesium and boron are studied in detail and are compared with that of cesium doping. The films are deposited in the temperature range 205 °C to 425 °C, with an accuracy of ± 5 °C. Structural, morphological, compositional, electrical and optical, characterisations are carried out with reference to film thickness. The gas sensing studies are conducted using an in-house designed glass chamber with gas inlet and outlet valves along with electrodes for the four probe V- I characterisation. Ageing effect due to interaction with humid ambient atmosphere on the films characteristics are studied for a period up to eight years. The modification take place by annealing of the films is also analysed in detail and explained. XRD, SEM, FESEM, EDX, UV-Vis, FTIR, and XPS are employed for the investigations.

The basic component of the spray pyrolysis solution is stannous chloride. 10 gm of $SnCl_2.2H_2O$ (Qualigens, GR) is dissolved in distilled, de-ionised water at 100 °C. A few ml. of conc. HCl (Merck GR grade) is added to dissolve residual precipitates if any. Subsequently isopropyl alcohol (Merck GR grade) is added in excess to form the spray solution of 90 ml. Doping with magnesium or boron is achieved by adding desired concentration of $MgCl_2$ or boric acid (both Qualigens, GR) to the starting solution. Dopant concentration selected for Mg is in the range of 0.3 wt. % to 7.5 wt. % and for boron in the range of 0.2 wt. % to 0.8 wt. %. Spraying the solution on chemically cleaned micro slides is done using glass atomiser having a minute nozzle of diameter 3×10^{-4}m with compressed air as carrier gas.

The thicknesses of the films determined using optical interferometry method and confirmed by Sloan Dektak 6M profilometer shows that the thickness are in the range 150 nm to 410 nm which is found to vary primarily due to deposition temperature and spray distance. For structural characterisation, X-ray diffractograms of both fresh and aged films are recorded using Rigaku MiniFlex 600 diffractometer using Cu Kα radiation. Grain size determined using Scherer equation is in the range of 37 nm to 43 nm for undoped films, where as of 36 - 51 nm for Mg doped and of 31 - 36 nm for

boron doped films. Major peaks corresponds to (110), (101), (200), (211), (301) and minor peaks corresponds to (220), (310), (321), (312) orientations of tetragonal cassiterite structure are obtained practically in all the films. The texture coefficients calculated for the films show that the undoped films are highly oriented in the (301) and (211) directions. By tuning deposition conditions with doping, the film can be made to grow preferentially in the (110) and (101) planes to show a higher magnitude of gas sensitivity. Standard deviations in intensity of planes are determined for the films and show that they are affected by deposition temperature and dopant concentrations. Micro strains are developed in the films during formation and are determined from Williamson-Hall plots reveal that, they are in the order of 10^{-3} for both Mg and boron doped films. The grain size determined from Williamson-Hall plots are slightly greater than that calculated from Scherrer formula. The lattice constants 'a' and 'c' are calculated and matched with the standard values (JCPDS card no. 21-1250) which shows that they are not affected by the present dopants or concentrations. This along with other measurements suggests that the Mg and B dopants do not replace lattice sites but prefer to disperse on the grain boundaries or the film surface.

The FTIR spectra of fresh samples taken by Perkin Elmer ATR FTIR show the vibrations of Sn-O, confirm the formation of tin oxide. However the absence of Cl vibrations in the spectra confirms that chlorine is not occluded in the film.

The instruments employed for SEM is Hitachi S 2400 and JEOL JSM 5610LV. The SEM micrographs of undoped films show that the grains are almost spherical in shape, uniformly spread in the area with voids in between them. On doping with Mg, the grains get modified to acquire a garden trowel shape. The distribution is uniform in wide area and voids also appear clearly. On boron doping, varied sized pebble shaped grains are formed. Boron doped films are tightly packed with lesser number of voids when compared to Mg doped films. The features slightly differ with deposition temperature and dopant concentration.

For composition analysis, EDX using JED 2201 is recorded. The EDX spectrum of samples shows the presence of Sn and O in undoped films. Presence of Mg and Boron is obtained in the corresponding films confirm that the dopants are incorporated in the films. The absence of chlorine in EDX data again confirms that the whole $SnCl_2$ gets converted to SnO_2 and the Cl_2 is escaped during pyrolytic reaction. The

quantitative analysis from EDX shows that the film lacks stoichiometry and there is oxygen deficiency in the bulk film leading to the formation of SnO_{2-x} (confirmed from XPS) which enhances the adsorption of oxygen on the surface. Hence on the surface, [O]/[Sn] ratio is greater than 2 for a certain range of x values which is greatly influenced by deposition parameters. About 85 – 95 % of added Mg is incorporated in to the film, where as only 45 – 65 % of the added boron is incorporated, which also is dependent on the dopant concentration and deposition temperature.

For optical studies, the UV-Visible spectra of the films are recorded using PerkinElmer Lambda 650 spectrometer in the range of 180 nm to 900 nm. For all the films deposited, the absorbance is very poor in the wavelength range of 400 nm to 900 nm. Hence it is concluded that the films are highly transparent to visible region. The absorbance shows ascend at wave lengths smaller than 400 nm and attains maximum in the range of 280 to 290 nm. The position of the peak slightly shifts with dopant concentration and deposition temperature which suggests that the deposition conditions modify the band gap energy of the material. The Tauc plot constructed from the data is extrapolated to obtain the X-intercept as the direct band gap energy. The band gap energy is found to increase continuously from 3.56 eV for deposition temperature 285 °C to 3.96 eV for deposition temperature 425 °C for undoped films. For Mg doped films, the E_g varies in the range of 3.67 eV and 4.26 eV. For boron doped films, the band gap energy varies in the range of 3.91 eV and 4.22 eV.

For detailed compositional analysis the XPS spectra of the films are taken employing Kratos Analytical -Axis Ultra. The wide scan spectrum is corrected with the adventitious C1s peak at 284.8 eV, for the peak shifts due to charging. The spectrum primarily consists of Sn 4d, Sn $3d_{5/2}$, Sn $3d_{3/2}$ and O 1s peaks confirms the presence of Sn and O. The high resolution scan of O 1s reveals that the binding energy is higher than the expected value (531.2 eV) which indicates that there are oxygen excess in the doped morphology. The asymmetry in the O 1s peak in high resolution scan required deconvolution. GL 30 deconvolution using ‘Vision process’ software suggests the presence of O^- as a major component along with smaller amount of adsorbed oxygen that exists on the grain surface of the sample in ambient atmosphere. The quantification analysis done from the area analysis of Sn and O peaks also confirms excess oxygen on the film surface. Mg KLL peak measured in the binding energy 304.8 eV along with

other characteristic binding energy peaks for Mg $2p_{3/2}$, Mg 2s at 50.7 eV and 91 eV respectively, provide definitive evidence for the presence of Mg in the doped samples. Similarly in boron doped films the presence of boron is ascertained by the peak obtained at 192.1 eV.

The a.c. conductivity studies of Mg doped films are done using QUADTECH 1920 precision LCR meter. The a.c. conductivity is very small up to a frequency of 500 KHz and shows a sharp increase above that. The gradual increase in a.c. conductivity with increase in frequency suggests that they must be related to the oxygen deficient stoichiometries present in the sample and the conduction of charge carriers among these phases due to hopping. The higher value of capacitance at lower frequency can be explained on the basis of interfacial or space charge polarization due to porosity as well as grain interface present in the films. With the increase in frequency the polarization decreases and then drops to a constant value owing to the fact that as the frequency of external field increases the hopping between metal ions of different types (Sn^{2+}, Sn^{4+}) and barriers cannot follow the changing field. It has also observed that the value of capacitance remains steady with the increase in dopant concentration. It may be due to the fact that the dielectric polarizability is not altered by small amount of doping. The decrease of loss factor at lower frequencies (up to 1 KHz) may be due to fact that the ions, or states at the grain boundaries, require more energy to transfer electrons whereas at higher frequencies grain conduction itself play a dominant role for which hopping require less energy.

For d.c. electrical characterisation, two probe measurements are carried out by Meco 45 digital multimeter and four-probe measurements are carried out by Keithley 2400 source meter. In the case of low resistive films, the resistance values obtained by four-probe method give significantly better values. The four probe resistances of undoped films are in the range of 0.8 to 1.5 kΩ where as for Mg doped film they are in the range of 1.5 to 3.5 KΩ and for boron doped films they are 1.5 to 1.9 kΩ. The resistance is found to increase with dopant concentration but decrease with deposition temperature. The resistance is also dependent on the grain size and thickness of the films.

On heating the films in ambient atmosphere up to 250 - 270 °C, the resistances of the films are found to decrease with increase in temperature, caused by increase in

carrier electrons showing up a semiconductor nature. But when the temperature is raised above 270 - 285 °C, the resistance starts to increase and gets saturated in the temperature range of 350 - 400 °C. The temperature range is governed by nature of dopant and amount. The increase in resistance at higher temperatures may be related to the oxygen adsorption at the enhanced temperature of the film. When the temperature is too high, further adsorption may not be possible or desorption of previously adsorbed oxygen takes place due to high excitation energy of the electrons and the resistance saturates. When the ambient gas is replaced by reducing gas like LPG or methane, a decrease in resistance is observed at temperatures above 280 °C for LPG and above 320 °C for methane. The reducing gas gets dissociated at higher temperature and reacts with adsorbed oxygen on the film surface producing H_2O, thereby liberating electrons for conduction, which decrease the resistance of the film. This phenomenon is exploited for gas detection. In the case of methane, being a stable gas requires higher temperature for dissociation.

The gas sensitivity (response) is defined as the ratio of change in film resistance in the presence of a test gas to its original resistance in atmospheric air, both measured at the operating temperature. For gas sensing studies, films deposited at temperatures 285, 325, 355, 385 and 425 °C are selected with Mg concentration in the range of 0.3 wt. % to 1.2 wt. % and boron concentration in the range of 0.2 wt. % to 0.8 wt. %, to compare with undoped films. It is ascertained that the gas sensitivity is a function of operating temperature. The films show only lesser response to LPG below an operating temperature of 280 °C but a maximum response is obtained around 350 °C. For methane gas, the response starts above an operating temperature of 320 °C and attains maximum at 385 °C. For both gases, measurements are carried out for 1000 ppm concentration (measured with ‘cosmic make LPG detector’) in air. The sensitivity studies in LPG are carried out at 350 °C but for methane at 350 °C and 385 °C. Undoped films have only very low sensitivity. Gas sensitivity of the films is found to vary with dopant, their concentration and the deposition temperature. Maximum sensitivity of 93 % is obtained for LPG with 0.6 wt. % Mg doped film deposited at 325 °C. When doped with boron, a maximum sensitivity of 82 % is obtained with 0.4 wt. % boron doped film deposited at 355 °C. These films have maximum intensities for the (101) and (110) reflections in the X-ray diffractograms and possess a distinctive feature of enriched oxygen adsorption on the film surface. In the case of methane gas, the

maximum sensitivity attained at 350 °C with Mg doping is only 13 %. At an elevated operating temperature of 385 °C, an appreciable sensor response of 52 % is obtained with Mg doped sample whereas 42 % with boron doped sample. Towards methane gas, the sensor responses of some of the doped films are lower than that obtained with undoped films. A good level of selectivity is achieved in the studied gases by properly setting the operating temperature. Grain size and initial resistance have direct impact on the response of the films. In Mg doped sensors, maximum sensitivity is attained with films having lesser grain size over the studied range. As the grain size is decreased the resistance of the film is found to increase to cause an enhanced gas sensing capability.

The response and recovery time of the films are also reported. Both are found to vary with dopants and composition of the films. The films doped with boron are found to have elevated values of these parameters when compared with Mg doped films. The response time is 59 seconds and recovery time is 71 seconds for 0.6 wt. % Mg doped film which is showing maximum sensitivity to LPG. For boron doped film with maximum sensitivity, the response time is 87 seconds and recovery time is 95 seconds when exposed to LPG. Both the parameters are a little larger when exposed to methane. The results are stable for multiple cycles of gas exposure and recovery.

For analysis of ageing effects, the films are stored in humid ambient atmospheres. They are loaded in sensing chamber at regular intervals and sensitivities are determined. The analyses have been carried out for 8 years with Mg doped films and 6 years with boron doped films. The sensors show a decrease in its gas response during ageing. The FESEM studies on aged films show growing surface modulation dependant on the duration of exposure to atmosphere, in particular humidity, which transformed the surface to form a melt away-like feature on the film. A thin coating can be observed over the surfaces, which partially cover up the surface grains. The Mg doped films are absolutely adhering on, without a symbol of lift off from the substrate even after prolonged ageing while the boron doped films are dissimilar and random peeling of films from the substrate starts roughly after four years of ageing.

The XRD peaks positions and texture of aged films are similar to that of fresh samples. It is concluded that the cassiterite structure has not affected due to ageing except that the background noise has increased to a certain extent. This may be as a result of stray reflections emanating from the transformed layer due to ageing

The film resistance is found to increase with long duration storage, and can be expressed by the relation

$$\mathbf{R_t = r_0 + r_0^{½} ln(t)}, \qquad \ldots\ldots\ldots\ldots (1)$$

where $\mathbf{r_0}$, is the initial resistance of the film, $\mathbf{R_t}$ after storage, where **t** is in months.

Etching of the film surface is done by Ar plasma to remove a layer of nearly 10 nm. The particles reappear as in the fresh samples. This demonstrates that no permanent change has occurred to the lower layers of the film. Annealing of the same set of sample in ambient air at deposition temperature regains the morphology as evidenced by FESEM images endorsing that the outer layers affected possibly by atmospheric humidity, can be readily get rid of from the surface to make the crystalline microstructure more sharp and faceted.

The FTIR absorption peaks observed in the aged Mg doped sensors at wave number 587 cm^{-1}, 764 cm^{-1} and 875 cm^{-1} confirm the δ_{OH} vibrations and suggests the formation of hydroxyl compound of tin. However the absence of OH mode of vibrations at 3000–3600 cm^{-1}, due to the in-plane deformation, suggests that the formed layer is marginal. Adsorption that involves direct H_2O linkage to SnO_2 is ruled out due to the absence of peak at 1620 –1640 cm^{-1}.

After Ar plasma etching in XPS analysis, the Sn 3d peaks become stronger accompanied by a decrease of C 1s peak. The changes can be associated with the removal of a thin surface layer of the film as a result of etching, substantiated by morphological change detected in the FESEM images. The deconvolution (GL 30) of high resolution O 1s peak resolve a component at 532.6 eV which corresponds the presence of –OH on the surface. On etching, the 532.6 eV peak disappears completely.

The analysis on ageing effect on the film sensitivities shows a slow decline in sensitivity on ageing. After a storage period of four years, it is seen that the response time has increased and the resistance variation profile is not smooth as in virgin sensor on exposure to the studied gases. On annealing the films at a temperature equal to their deposition temperature recover the previous sensitivity magnitudes. The percentage decrease in sensitivity due to ageing is almost uniform irrespective of film deposition condition or initial sensitivity which is higher for boron doped films when compared with Mg doped films.

The sensor response results are compared with Cs doped SnO_2 films developed in the initial stages of this work. It is found that the smaller the ionic size of dopant, the

lesser the dopant concentration required to achieve maximum gas response. Both response and recovery durations are longer for films doped with boron (lesser in ionic radius). The durations decrease for films doped with magnesium (ionic radius similar to that of Sn), whereas show higher durations for films doped with Cs (larger ionic size). The Mg doped films possess more stability in terms of adhesion to substrate and gas sensitivity on ageing whereas possess least stability by boron doped films.

The proposed thesis "*Microstructural and compositional aspects owing to Mg and B additives in spray deposited SnO_2 thin films for enhanced LPG and Methane sensing*" consists of 6 chapters and appendices. The first chapter comprises of a general introduction in which the relevance of the topic and the literature is reviewed. The principles and theory on which the work is based, together with experimental techniques are discussed in the second chapter. Detailed reports on the sensing studies of Mg doped fresh and aged films are presented in the third chapter along with a study on undoped films. In fourth chapter, the sensing analysis reports on fresh and aged boron doped films are presented. The fifth chapter includes the sensitivity reports of Cs doped films and their ageing study. In this chapter the results of Mg, B and Cs doped films are compared. The results of the investigation are summarised in the sixth chapter and the scope for future work are also discussed.

Research Publications to Date (Published /under Review)

I. Peer Reviewed International Journals

1) Influence of Cs doping in spray deposited SnO_2 thin films for LPG sensors, Boben Thomas, **Benoy Skariah** & Radha K.K., Sensors and Actuators B 133 **(2008)** 404-413, doi: 10.1016/j.snb.2008.02.050.

2) Deepa S., Anisha Joseph, **Benoy Skariah** and Boben Thomas, Gas sensing properties of magnesium doped SnO_2 thin films in relation to AC conduction, American Institute of Physics, Conference Proceedings 1576 (**2014**) 49-51, doi: 10.1063/1.4861977

3) **Benoy Skariah** and Boben Thomas, Magnesium doping to enrich oxygen adsorption for LPG sensing in spray pyrolysed SnO_2 films, J. Sensor and Sensor Systems **(**under review**).**

4) **Benoy Skariah**, Johns Naduvath and Boben Thomas, Effect of ageing on microstructure and gas-sensing properties of spray pyrolysed magnesium doped SnO_2 films, Sensors and Actuators B (under review).

5) **Benoy Skariah** and Boben Thomas, Ageing effects on spray pyrolysed B:SnO_2 thin Films for LPG sensing, Optics'14, AIP conf. proc., (accepted**)**.

6) **Benoy Skariah** and Boben Thomas, Structural and surface analysis of B:SnO_2 thin films for gas sensing, Review of research (communicated**)**.

II. Technical Excellance Award

7) Oxygen annealing effects on LPG response of SnO_2:Cs thin films, Radha K.K., **Benoy Skariah** and Boben Thomas, Proc. of ISRS'06, **2006**, IIT Chennai.

III. National Conference Proceedings

8) Influence of Mg additive on the Gas response in spray deposited polycrystalline SnO_2 at LPG ambience, Boben Thomas, **Benoy Skariah** & Radha K.K., Proc. of DAE SSPS 49, **2004**, 526-527, Amritsar.

9) Effect of additives on the gas sensing behavior of SnO_2 thin films, **Benoy Skariah,** Radha K.K. & Boben Thomas , Proc. Of the DAE SSPS 51, **2006**, 457-458, Bhopal.

10) Response of SnO_2:Mg films towards LPG and methane, **Benoy Skariah,** Radha K.K. & Boben Thomas, Proc. of National conference on smart electronics, 95-96, **2007**, CMET, Thrissur.

11) Deposition and characterization of Boron doped SnO_2 sensors, **Benoy Skariah,** Radha K.K., Boben Thomas, Proc. of 12th National conference on Physics and technology of sensors, **2007**, 183 – 185, BARC, Mumbai.

12) Sensitivity of Boron loaded Tin oxide films towards methane, **Benoy Skariah** and Boben Thomas, Proc. of the DAE SSPS 52, **2007**, Mysore.

13) Structural and electrical characterization of boron activated tin oxide films for methane ambience sensing, **Benoy Skariah.** and Boben Thomas, Proc. of the National workshop on quantum confined systems and nanoscale device, **2009**, 99-104, Pala.

IV. Publications outside thesis content

14) Resistance variation of copper doped SnO_2 films in petroleum gas ambient, **Benoy Skariah** , Radha K.K & Boben Thomas, Proc. of ISRS'06, **2006**, IIT Chennai
15) Structural and gas sensing properties of SnO_2:La sprayed thin film, Radha K.K., **Benoy Skariah,** Boben Thomas, Proc. of 12th NSPTS, **2007**,186, BARC, Mumbai
16) Gas sensing characteristics of Mn doped SnO_2 thin films, Radha K.K., **Benoy Skariah** & Boben Thomas, Proc. of National conference on smart electronics, **2007**, 99, CMET Thrissur.
17) Gas micro-sensor alloy SnO_2:La_2O_3 having stability for detecting LPG, Boben Thomas, Radha K.K., Renjith Mark George & **Benoy Skariah**, Proc. of DAE SSPS 49, **2004**, 468-469, Amritsar

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